

ELECTROCHEMICAL STUDIES OF OXYGEN ACTIVITY DURING THE OXIDATIVE COUPLING OF METHANE

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When studying the kinetics of heterogeneous catalytic reactions, it is crucial to be able to measure the surface concentrations under actual reaction conditions. Unfortunately, there are virtually no techniques currently available which permit the measurement of these surface concentrations under the atmospheric pressures and high temperatures that most catalytic reactions occur. In this work we report the measurement of the thermodynamic activity of oxygen on the surface of a Li promoted MgO catalyst during the oxidative coupling of methane. This measurement provides additional information which may be utilized in the description of the different reactions responsible for the formation of the coupling and deep oxidation products.

The measurement of the thermodynamic activity of oxygen on catalytic metal films was first reported in 1976 by Vayenas and Saltsburg in a study of the oxidation of SO_2 over Pt (1,2). An electrochemical cell consisting of two porous catalytic Pt films separated by an oxide conducting solid electrolyte was utilized in these oxygen activity measurements. It has been shown that the oxygen activity on the metal films is related to the measured EMF through the Nernst equation. The surface oxygen activity is directly related to the surface oxygen concentration and its measurement subsequently provides information about reactions involving the surface oxygen.

This technique has been extended by McKown (3) so that the thermodynamic activity of oxygen on metal oxide catalysts may be measured under reaction conditions. It was demonstrated that an electrochemical based oxygen sensor similar to that utilized by Vayenas and Saltsburg was capable of measuring a mobile oxygen species on the oxide catalyst surface. In this manner, the effect that the oxidative coupling of methane reaction is having on the surface oxygen species may be monitored.

The oxygen activity on a Li promoted MgO catalyst was monitored along with overall conversion and selectivity for a variety of reaction conditions. It was found that in the presence of the coupling reaction, the measured surface oxygen activity was always lower than its equilibrium value. Furthermore, the extent of deviation from oxygen gas-surface was observed to be a function of reaction conditions. It was deduced that a reaction involving the mobile surface oxygen was responsible for the lowered steady state amount of surface oxygen. The magnitude of this deviation from equilibrium between oxygen in the gas and on the catalyst surface must then be related to the rate of reaction depleting the mobile surface oxygen.

As the selectivity for the formation of the C_2 products increased, the deviation from equilibrium between oxygen in the gas and oxygen on the catalyst surface was also observed to increase. Since an increased deviation from gas-surface equilibrium indicates an increased rate of reaction involving surface oxygen, it was concluded that the production of the C_2 products, C_2H_4 and C_2H_6 , must involve a mobile surface oxygen species. Similar arguments can be employed to deduce that the C_1 products, CO and CO_2 , must be formed primarily by a reaction with oxygen from the gas.

Lunsford et. al. (4,5) were able to characterize the active center responsible for the activation of the CH_4 molecule in the Li promoted MgO catalyst using ESR. We have combined their active site characterization with our oxygen activity measurements in a mechanism which is based heavily on experimental observations.

We have demonstrated the ability to measure a quantity which is directly related to the surface oxygen concentration on a metal oxide catalyst under actual reaction conditions. This technique has provided vital information about the types of reactions responsible for the selectivity in the oxidative coupling of methane.

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